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PATENT SPECIFICATION

DRAWINGS ATTACHED

994,789



Date of Application and filing Complete Specification Sept. 29, 1961.

No. 35091/61.

Application made in Germany (No. B59607 IVd/39c) on Oct. 1, 1960.

Application made in Germany (No. B63868 IVd/39c) on Sept. 1, 1961.

Complete Specification Published June 10, 1965.

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The inventor of this invention in the sense of being the actual deviser thereof within the meaning of Section 16 of the Patents Act 1949 is Hans-Werner Otto, a citizen of Germany and a resident of 163 Sternstrasse Ludwigshafen/Rhein, Germany.

Index at acceptance: —B1 X3X6; C3 P(7D2A1,, 7P1D, 7P1E5, 7P2A4, 7P3, 7P6A, 7P6B, 7P6X, 8D1A, 8D2A, 8K8, 8P1E5, 8P2A1, 8P2A4, 8P6A, 8P6B, 8P6X); B1 C(1, 5, 10, 19F1)

Int. Cl.: —C 08 f//B 01 f

COMPLETE SPECIFICATION

Process and Apparatus for the Continuous Polymerisation of Ethylenically Unsaturated Polymerisable Compounds

We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company of Ludwigshafen/Rhein, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process and an apparatus for the continuous polymerisation of ethylenically unsaturated polymerisable compounds, the material to be polymerised being mixed by special means.

It is known to polymerise monovinylaromatic compounds continuously, if desired with the addition of not more than 25% of other copolymerisable olefinically unsaturated monomers, in a polymerisation tower having a plurality of zones of differing temperature increasing with loss of height, the highest having a temperature of at least 85° and preferably 130° C. The polymerisable composition is fed to the upper end of the tower and stirred by several blades arranged along the longitudinal axis of the tower but rotating transversely to the longitudinal axis, so that the composition being polymerised is not whirled up. The hot plasticised composition containing at least 40% by weight of polymer is withdrawn at the lower end of the tower.

According to the process of the present invention ethylenically unsaturated polymerisable compounds can be advantageously polymerised continuously in a cylindrical reaction vessel when the material to be polymerised is agitated using a plurality of perforated

plates sieve plates or sieves mounted transversely on a shaft reciprocating in the direction of the longitudinal axis of the reaction vessel, and the ratio (φ) of the average distance between the plate on the shaft to the length of the stroke lies between $\varphi=1:1$ and $\varphi=1:0.1$.

Examples of ethylenically unsaturated polymerisable compounds are vinylaromatic compounds, such as styrene, α -methylstyrene and o-chlorostyrene; vinyl halides, such as vinyl fluoride, vinyl chloride, vinylidene chloride and vinylidene fluoride; acrylic compounds, such as acrylic and methacrylic acids and their methyl, ethyl, propyl, isopropyl, cyclohexyl and 2-ethylhexyl esters as well as acrylonitrile, methacrylonitrile, acrylamide and methacrylamide; vinyl esters, such as vinyl acetate, propionate and butyrate; as well as diolefines, such as butadiene, 2-chlorobutadiene and isoprene.

Such monomers may be polymerised for example individually, in the block, or in admixture with each other, if desired in the presence of the usual polymerisation catalysts, such as peroxides or azo-bis-nitriles, and at the usual polymerisation temperatures, until the proportion of polymer in the polymerising composition is at the most 60% by weight, preferably not more than 40% by weight. It is generally advantageous for the polymerising composition in the polymerisation tower to exhibit a temperature gradient the temperature at the inlet opening of the tower being suitably up to 120° C lower than at the outlet opening. It is of special advantage to arrange in series a plurality of such

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towers, if desired of different sizes, in which different polymerisation temperatures may be set up. In some cases, for example in the polymerisation of vinyl halides, it is convenient to carry out the process according to this invention under increased pressure.

According to another embodiment of the process, the monomers of the above-mentioned kind may be polymerised with advantage in dispersion or solution, if desired with the addition of the usual dispersing agents or emulsifiers and with the use of the conventional polymerisation catalysts at the usual temperatures. In the case of an emulsion polymerisation, the monomers, water, emulsifier and catalysts may be introduced, for example separately, into the polymerisation tower and mixed and emulsified at the point of entry. Ready-made emulsions of the monomers, emulsifier and catalysts may, however, also be supplied to the polymerisation tower. If polymerisation is to be effected in dispersion or solution, it may be completed in one or conveniently in a plurality of successive towers.

In the process, the speed of the stroke of the perforated plates may be varied in dependence on the viscosity of the composition being polymerised. In the case of block polymerisation it is advantageously between 1 and 120 cm, preferably between 6 and 60 cm per minute, in the case of emulsion polymerisation advantageously between 10 and 1200 cm, preferably between 30 and 600 cm per minute, and in the case of solution polymerisation advantageously between 1 and 120 cm, preferably between 6 and 60 cm per minute. In special cases, however, very high stroke-speeds for example of more than 3000 cm per minute, may be of advantage.

The invention will now be described in greater detail with reference to the accompanying drawings.

Figure 1 shows diagrammatically an apparatus according to this invention for carrying out the polymerisation process. The apparatus comprises a cylindrical reaction vessel 1 (tower), which is surrounded by a jacket 4 through which a heating or cooling medium can be passed by means of pipes 7 and 8. Pipes 10 and 9 respectively are provided at the ends of the tower for the supply of the composition to be polymerised and the discharge of the polymerised composition. These pipes may be as shown or may also be arranged laterally. A reflux condenser may be connected to the pipe 11. The ratio (w), of the length of tower 1 to its diameter is advantageously between $w=250:1$ and $w=10:1$, preferably between $w=100:1$ and $w=20:1$. Shaft 2 is mounted in bearings 5 and 6 in the direction of the longitudinal axis of tower 1. Perforated plates 3 are mounted on shaft 2.

Shaft 2 can be reciprocated vertically in

a ratio (v) of the average distance between the plates on the shaft to the length of stroke between $v=1:1$ and $v=1:0.1$, preferably between $v=1:0.8$ and $v=1:0.5$. It may be arranged centrally or eccentrically.

The distance between the edge of the plates and the wall of the vessel is advantageously 0.1 to 5 cm, preferably 0.5 to 2 cm. The ratio (x) of the average distance between the plates to the inner radius of the tower 1 is advantageously between $x=1:1$ and $x=1:100$, preferably between $x=1:2$ and $x=1:10$. The shaft 2 and the plates 3 may be made hollow with advantage and the shaft provided with an inlet and an outlet for a heating or cooling medium. In this case the heating or cooling medium may conveniently be introduced through pipes 12 (Figure 3) through the shaft 2 and distributed radially into the perforated plates through pipes 13 branched off from the pipe 12. The medium emerging from the ends of the pipes 13 flows down the annular column between the pipe 12 and the shaft 2 in the direction of the arrows, and is drained off by conventional means at the bottom of the reaction vessel 1 (tower). The composition to be polymerised flows through vertical ducts 17, which form the perforations in the plate 3. Figures 3 and 4 show a vertical and horizontal section through the point at which one of the perforated plates 3 is mounted on the shaft 2; and illustrate one possible arrangement of tubes 12 and 13. The plates are generally equal distances apart. In this case the average distance between the plates is equal to the distance between the individual plates. When the viscosity of the composition to be polymerised increases considerably in the reaction vessel, it may be of advantage for the distance between the plates to increase in the direction of movement of the composition being polymerised. In this case the average distance between the plates is the arithmetical mean of the various distances between the plates. The number and diameter of the holes in the perforated plates 3 depends primarily on the viscosity of the composition to be polymerised in the apparatus. In the case of a very viscous composition the holes must be made larger, or there must be more per plate, and conversely if the viscosity is small. Obviously, in each case the number and diameter of the holes must be adjusted according to the viscosity of the composition being handled. The holes may be arranged in the plate 3 for example radially in circles (cf. Figure 2a) or staggered (cf. Figure 2b).

It is especially advantageous to subdivide the cylindrical reaction vessel into a plurality of chambers by rigidly mounted perforated plates 14 arranged transversely to the longitudinal axis, or by stilling chambers each formed by two perforated plates 14

rigidly arranged transversely to the longitudinal axis (see Figure 6) and which may be charged with packing 15 (see Figure 7). This subdivision may alternatively be effected for example so that between each two perforated plates 3 a perforated plate is rigidly arranged transversely to the longitudinal axis as shown in Figure 5. The rigidly arranged plates may with advantage be made hollow and heated or cooled by passing a heat-exchange medium through them. The ducting of this medium through the plates may be effected in any convenient manner, for example by feeding the hollow plates with medium supplied via the hollow wall of the reaction vessel (schematically illustrated by the arrows 18 in Figure 5), or via inlet and outlet pipes 16.

It is obvious that the perforations need not be circular and their shape is not important for the present process. Instead of perforated plates, there may also be used, for example, sieve plates or sieves with equal or differing mesh widths.

The dimensions of the apparatus according to this invention and also the number of perforated plates on the shaft 2 depend on the desired throughput. Conventional materials for the construction of chemical apparatus are suitable as materials for the apparatus according to this invention.

It is advantage of the process that the polymerisation temperature can be very well controlled because the ratio of reaction volume to heat-exchange is very favourable. A further advantage is that the actual residence period of the monomers is not greatly different from the average residence period. In the case of solution or block polymerisation, the molecular weight distribution of the polymers can be adjusted within wide limits by varying the dimensions of the apparatus. In emulsion polymerisation, dispersions can be prepared with the desired particle size distribution within wide limits. The properties of the polymers obtained can therefore be influenced to a large extent.

The invention is illustrated by, but not limited to, the following Examples, in which parts are parts by weight.

EXAMPLE 1

The apparatus used is one similar to that shown in Figure 1, and has a volume of 800 ml. 275 gms. per hour of an emulsion of 1000 parts of styrene, 2100 parts of water, 20 parts of a sodium salt of paraffin sulphonic acids with 12 to 18 carbon atoms and 3 parts of potassium persulphate is supplied continuously through pipe 10. The temperature of the polymerising composition is kept at 60° C by a heating medium flowing through heating jacket 4. The frequency of stroke of shaft 2 with perforated plates 6 is 60 strokes per minute. 275 gms. of a polystyrene dispersion containing 29.7% by

weight of polystyrene of the K-value 115 is continuously withdrawn per hour through pipe 9. The polystyrene particles have a particle size of 0.1 to 0.2 micron. Conversion amounts to 92%. If the apparatus were 1000 times larger, as it would be on a technical scale, the throughput would obviously be in Kg.

The ratio (w) of the length of the reaction vessel used to its diameter is $W=20:1$, the ratio (x) of the distance between the plates to the inner radius of the reaction vessel is $x=1:1.2$ and the ratio (v) of the mean distance of the plates 3 from each other to the length of the stroke of the plates is $v=2.5:1$. The distance between the edge of the plates and the wall of the reaction vessel is 0.1 cm.

EXAMPLE 2

400 gms per hour of an emulsion of 980 parts of butyl acrylate, 20 parts of acrylic acid, 1600 parts of water, 20 parts of a commercial aryl sulphonate and 5 parts of a commercial persulphate is continuously polymerised at 75° C in the apparatus described in Example 1. The conversion is 92%.

A dispersion is obtained which contains 35.5% by weight of a copolymer of butyl acrylate and acrylic acid of the K-value 80 to 85. The dispersion has a surface tension of 36.00 dynes per cm.

EXAMPLE 3

200 gms per hour of a mixture of 500 grams of styrene, 500 grams of toluene and 5 grams of azo-di-isobutyro-dinitrile is continuously polymerised at a temperature of 80° C in the apparatus described in Example 1 having a volume of 800 ml. The stroke frequency is 20 strokes per minute.

An about 30% solution of polystyrene with the k-value 21 in toluene is obtained in which some monomeric styrene is present. The space time yield is 95 grams of polystyrene per litre of reaction space per hour.

EXAMPLE 4

400 gms per hour of styrene is continuously polymerised in an apparatus as in Example 1 with a volume of 800 ml at a temperature of 130° C up to a conversion of 35%.

The K-value of the product obtained is 62. The stroke frequency is 26 strokes per minute.

Polymerisation is then completed in conventional way, for example in a tower without insertions.

EXAMPLE 5

320 gms. per hour of an emulsion of 980 parts of butyl acrylate, 20 parts of acrylic acid, 100 parts of water, 50 parts of a sulphonated condensation product of 1 mole of fatty alcohol ($C_{16}-C_{18}$) with 25 moles of

ethylene oxide and 5 parts of potassium persulphate is polymerised continuously at 80° C in an apparatus as in Example 1.

5 A dispersion is obtained which contains 49.5% of a copolymer of butyl acrylate and acrylic acid and having the K-value 75 to 80. The surface tension is 40.9 dynes per cm.

WHAT WE CLAIM IS:—

10 1. A process for the continuous polymerisation of ethylenically unsaturated polymerisable compounds in a cylindrical reaction vessel wherein the material being polymerised is agitated by means of a plurality of perforated plates sieve plates or sieves, mounted transversely on a shaft reciprocated in the direction of the longitudinal axis of the reaction vessel, the ratio (v) of the average distance between the plates on the shaft to the length of the stroke of the same lies between $v=1:1$ and $v=1:0.1$.

20 2. The process for the continuous polymerisation of ethylenically unsaturated polymerisable compounds substantially as described in any of the foregoing Examples.

25 3. Apparatus for carrying out the process claimed in claim 1 comprising a cylindrical reaction vessel, a shaft mounted in the direction of the longitudinal axis thereof, and a plurality of perforated plates sieve plates, or sieves mounted on said shaft transversely to said axis, said shaft and plates being capable of reciprocatory movement longitudinally to said vessel and the ratio (v) of the mean spacing of the plates on the shaft to the length of stroke of said reciprocatory movement being between $v=1:1$ and $v=1:0.1$, and the ratio (x) of the mean distance between the plates to the inner radius of the

reaction vessel lying between $x=1:1$ and $x=1:100$.

40 4. Apparatus as claimed in claim 3, wherein the shaft and the perforated plates are hollow and are provided with pipes through which a heating or cooling medium can be passed.

45 5. Apparatus as claimed in claim 3 or 4 wherein other perforated plates are rigidly mounted in the cylindrical walls of the reaction vessel transversely to the shaft in the reaction vessel.

50 6. Apparatus as claimed in claim 5 wherein one of said rigidly mounted plates is arranged on each side of a perforated plate mounted on the shaft.

55 7. Apparatus as claimed in claim 5 or 6 wherein two of said rigidly mounted plates are arranged adjacent to each other.

60 8. Apparatus as claimed in claim 7 wherein the space between said adjacent rigidly mounted plates is charged with packing.

65 9. Apparatus as claimed in any of claims 5 to 8 wherein the rigidly mounted plates are hollow and means are provided for supplying a heating or cooling medium to the interior of the same.

70 10. Apparatus as claimed in claim 3 substantially as herein described with reference to Figures 1 and 2, Figures 3 and 4, Figure 5, Figure 6 or Figure 7 of the accompanying drawings.

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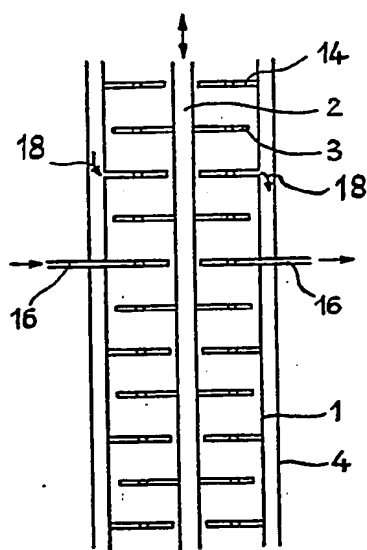
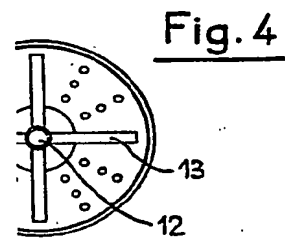
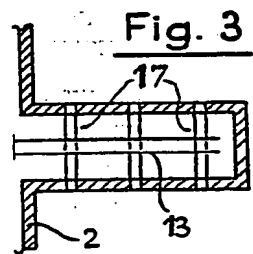
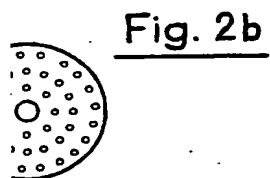
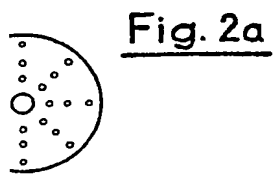


Fig. 5

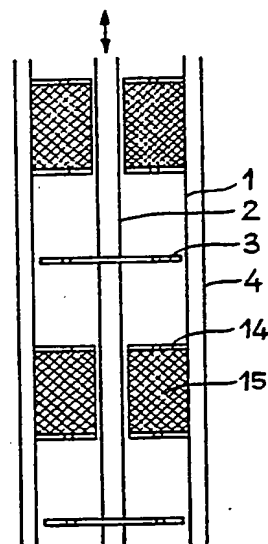


Fig. 7

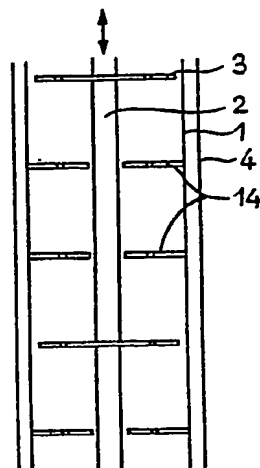
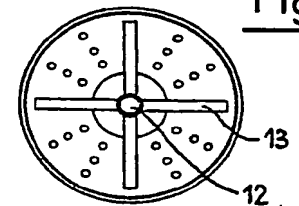
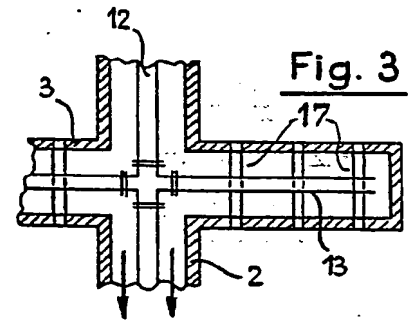
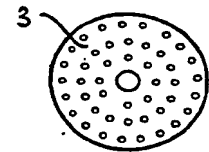
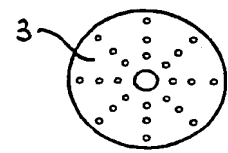
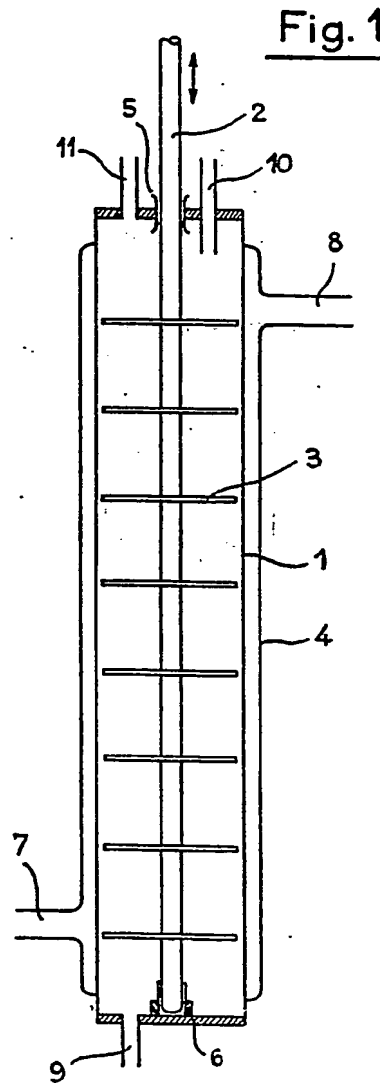


Fig. 6



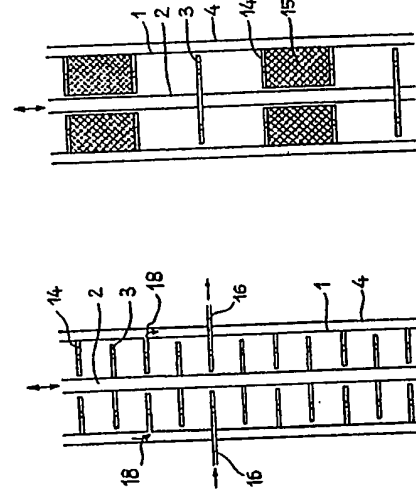
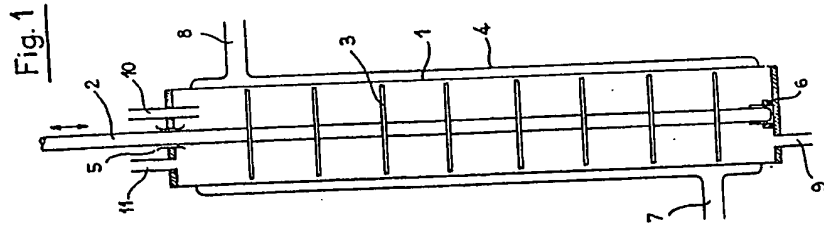


Fig. 5

Fig. 6

Fig. 7

Fig. 2a

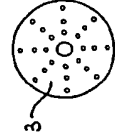


Fig. 2b

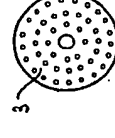


Fig. 3

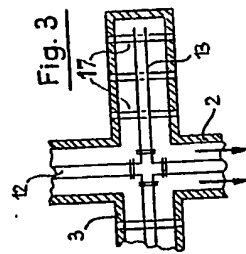


Fig. 4

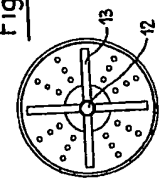


Fig. 6

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